CHEM 8410_6410_4410 Spring 2020 – Mid-Term Exam 1
02-18-20

Time: 10:00 am – 11:15 am

Student Name: ______________________________

Student Number: ______________________________

Instructor:	Prof. Andreana
Room #:	BO 2059

CHEM 8410_6410_4410 – Organic Synthesis

Mid-Term Exam 1

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100 Points - Total

1. **Problem 1:** Please provide mechanisms for 6 of the following 13 named reactions: **(30 Points)** - * indicates this named reaction **MUST** be one of your 6.

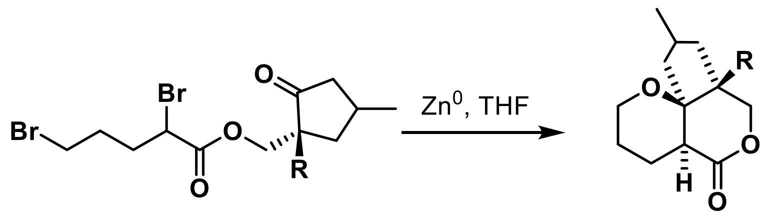
    1. Baylis-Hillman Reaction
    2. Baeyer Villiger Reaction
    3. Bamford-Stephens Reaction
    4. Barton -McCombie Reaction
    5. Brook Rearrangement
    6. Claisen Rearrangement
    7. Chichibabin Reaction
    8. Biginelli Reaction
    9. Bishler-Napierlski Reaction

    *10. Bucherer-Bergs Reaction

    11. Beckmann Rearrangement
    12. Bechamp Reduction
    13. Canizzaro Reaction

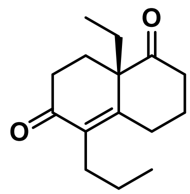
Answers:

Problem 2: Provide a mechanism that accounts for observed stereochemistry of the illustrated transformation. (**10 PTS**)



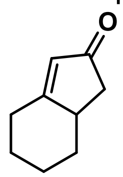
Answers:

Problem 3. Please prepare the compound noted below from starting materials that contain four carbons or less and cyclohexanone. **(10 Points)**



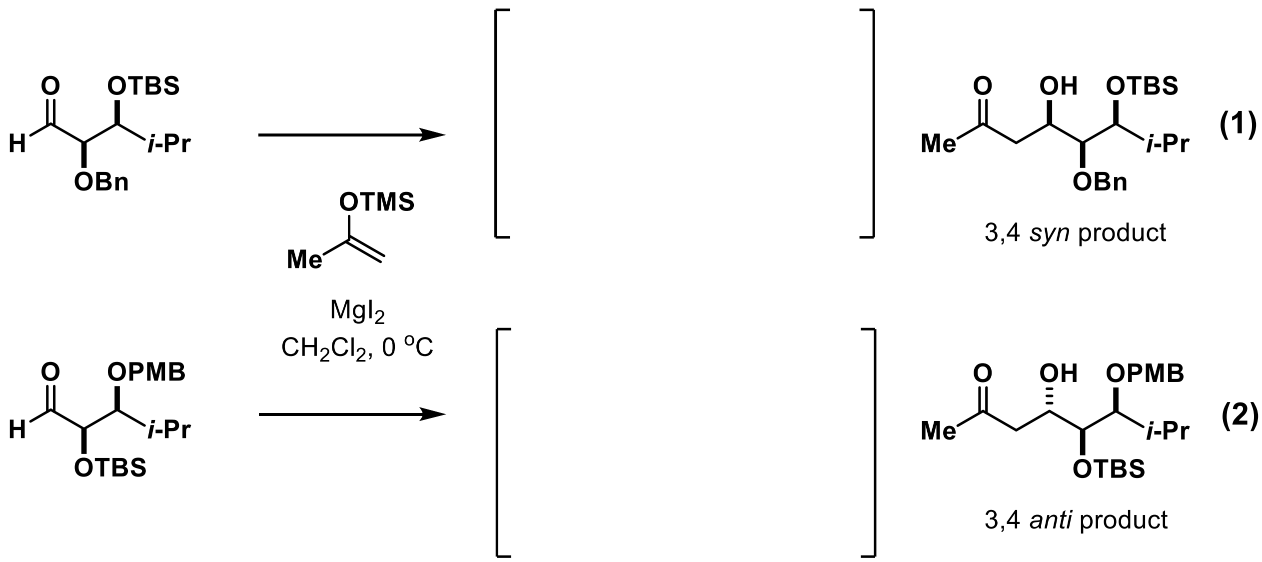
Answers:

Problem 4: Show how you would synthesize the following molecule. Use and show retro-synthetic analysis to break the pertinent bonds. Provide mechanisms for every step you use. As a hint, start with cyclohexanone and some other compound of your choice. (**10 Points**)



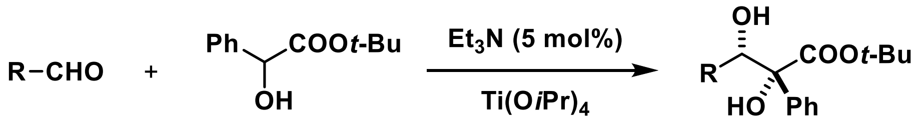
Answer:

Problem 5. The two illustrated MgI_2–promoted Mukaiyama aldol reactions occur with high diastereoselectivity (Eq 1 & 2). In contrast, only poor selectivity is observed in both reactions when MgI_2 is replaced with BF_3•OEt_2. Provide a transition state model that explains the formation of the 3,4 *syn* product in (Eq 1) and the 3,4 *anti* product in (Eq 2). Assume that the Bn and PMB protecting groups are chemically equivalent. **(10 Points).**



When the chelating protecting group is in the alpha position (Eq 1), a five member chelate is formed and incoming nucleophile attacks the *si*-face opposite to the R group (TS-1). In contrast, a six-membered chelate is formed when the chelating protecting group is in the beta position and the nucleophile approaches from the face away from both the OP and R groups. The observation that BF_3•OEt_2 gives poor selectivity implies that the reaction is not simply under Felkin control, as one may predict for Eq 2.

Problem 6: Rationalize the *syn*-selectivity of the following reaction with a clear 3-D representation of the Zimmerman-Traxler transition state. (**15 PTS**)



R	yield (%)	ratio (*syn*/*anti*)
Me	70	55:45
Et	75	79:21
i-Pr	78	94:06

Problem 7: Provide clear 3D depictions of the transition states for the following hydroborations. Specifically point out each factor responsible for the observed turnover in selectivity (Tatsuda, *TL*, **1991**, 6015). (**15 PTS**)